Isomerization of Diphenyl Polyenes. Part VI. Properties of 1,8-Diphenyl-1,3,5,7-octatetraene Fluorescence in Poly(vinyl alcohol) and other Polymer Films

A. Kawski, A. Kubicki, B. Kukliński, and G. Piszczek

Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk,
80-952 Gdańsk, Poland

Z. Naturforsch. **48a**, 947–954 (1993); received July 14, 1993

Absorption, fluorescence and emission anisotropy spectra of 1,8-diphenyl-1,3,5,7-octatetraene (DPO) in non-heated and heated poly(vinyl alcohol) (PVA) films were measured at 296 and 87 K. Similar spectra to those of DPO in PVA heated to 423 K were observed for DPO in polymer films: poly(vinyl chloride) (PVCh), poly(vinyl formal) (PVF) and ethylacetate (EtA). Unusual photophysical properties of DPO fluorescence occur only in non-heated PVA. These are the increase in the absorbance and quantum yield at temperatures above 358 K and the change in the emission anisotropy, *r*, due to softening or stiffening of the PVA film. For DPO in PVCh and EtA, high values of *r*, close to 0.4, are observed (0.391 and 0.389, respectively), thus manifesting the stiffening of the microenvironment around the DPO molecule in these polymers. In the case of DPO in non-heated PVA film, strong temperature dependence of the intensity distribution in the fluorescence band and double exponential emission decay are observed. This proves that the fluorescence originates from two conformers: all-*trans* and s-*cis*.

1. Introduction

The electronic structure of linear polyenes, Ph–$(CH=CH)_n$–Ph, was the object of numerous experimental and theoretical investigations [1, 2]. By investigating a series of diphenyl polyenes ($n = 2, 3, 4$), Hudson and Kohler have shown [3, 4] for all-*trans*-diphenyl-1,3,5,7-octatetraene ($n=4$) (DPO), that the lowest excited singlet state is the optically forbidden $2^1A_g(S_1)$ state which lines below the optically allowed $1^1B_u(S_2)$ state. The $2^1A_g \leftarrow 1^1A_g$ transition is lower in energy [1, 2] and gains intensity from the $1^1B_u \leftarrow 1^1A_g$ transition by vibronic coupling [5, 6]. For all diphenyl polyenes, $n=2, 3, 4$, the transition moment is parallel to the long molecular axis [7, 8].

Electro-optical absorption studies of centro-symmetric molecules, e.g. of DPO, enabled the polarizability and electric dipole moment to be determined in the excited state [9, 10].

The manifestations of these unusual properties of diphenyl polyenes can frequently be observed. For example, absorption and fluorescence spectra reveal poor mirror-image symmetry and a large Stokes shift. The radiative rate parameter $k_F = \Phi_F/\tau$ (where Φ_F and τ are the fluorescence yield and decay time, respectively) is smaller than the parameter k_F^c calculated from the integrated absorption spectrum, and for DPO the ratio $R = k_F^c/k_F$ amounts to 22 [11–13]. Low quantum yields, Φ_F, and long lifetimes, τ, of DPO are observed in liquid solvents. Chattopadhyay et al. [14] obtained $\Phi_F = 0.085$ and $\tau = 6.7$ ns, $\Phi_F = 0.088$ and $\tau = 7.1$ ns and $\Phi_F = 0.091$ and $\tau = 6.8$ ns in cyclohexane, benzene and methanol, respectively. Recently, unusual behaviour of the DPO absorbance and quantum yield was observed in poly(vinyl alcohol) (PVA) films at temperatures above 358 K [15, 16]. At such temperatures the absorbance and quantum yield strongly increase. This effect is irreversible, i.e. upon cooling to room temperature the sample retains both high absorbance and fluorescence quantum yield. Similar behaviour was observed for 1,6-diphenyl-1,3,5-hexatriene (DPH) in PVA. In this case, however, the effect was slightly weaker [17, 18].

In the present paper, further studies on the above effect are reported for DPO molecules in PVA and other polymers such as poly(vinyl chloride) (PVCh), poly(vinyl formal) (PVF) and ethyl acetate (EtA).

2. Experimental

DPO from Aldrich Chemical Company Inc., Steinheim, Germany, was used without further purification.

Reprint requests to Prof. Dr. Alfons Kawski, University of Gdańsk, Institute of Experimental Physics, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

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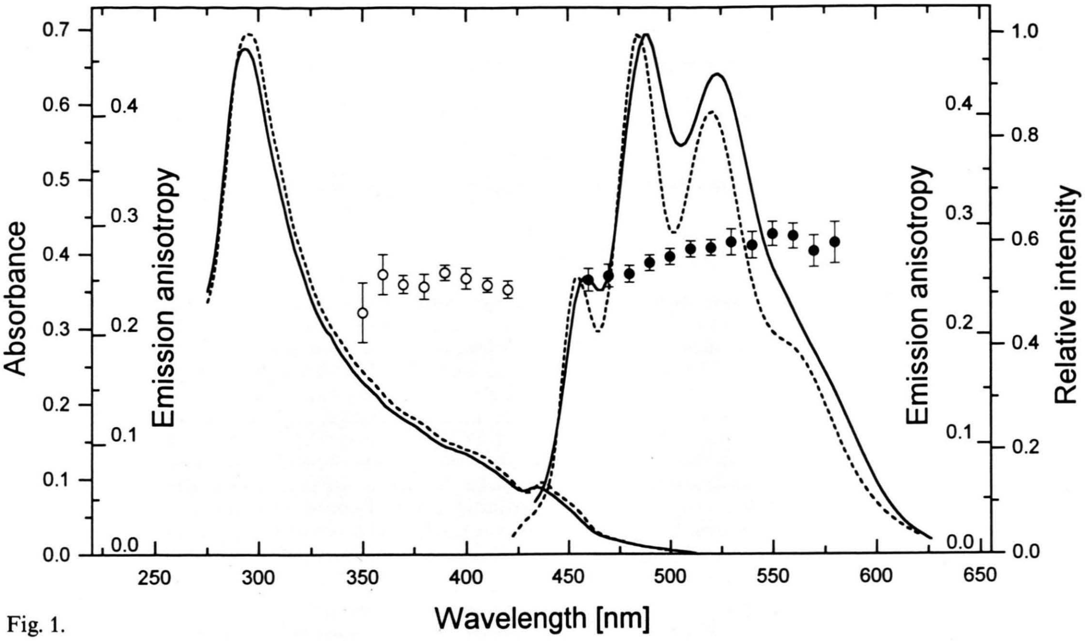

Fig. 1.

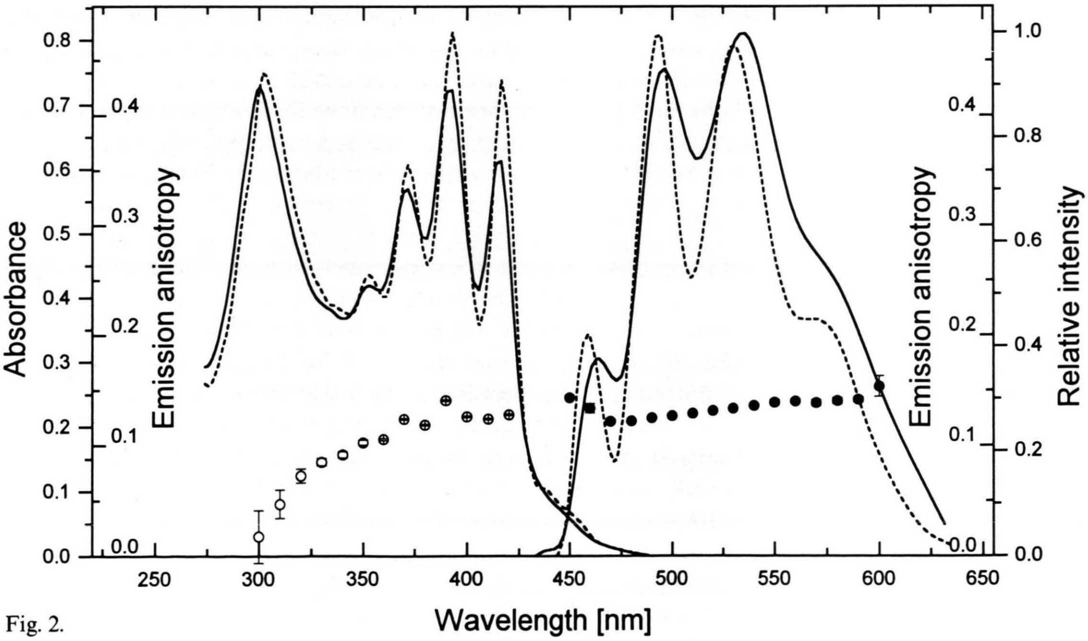

Fig. 2.

Figs. 1–3. Absorption and fluorescence spectra of DPO in PVA film before heating (Fig. 1), after heating to 373 K (Fig. 2) and after heating to 423 K (Fig. 3), measured at 296 K (solid line) and 85 K (dashed line). The fluorescence and emission anisotropy (●) spectra were obtained for $\lambda_{exc} = 390$ nm. o denote the emission anisotropy at $\lambda_{obs} = 430$ nm for various λ_{exc}.

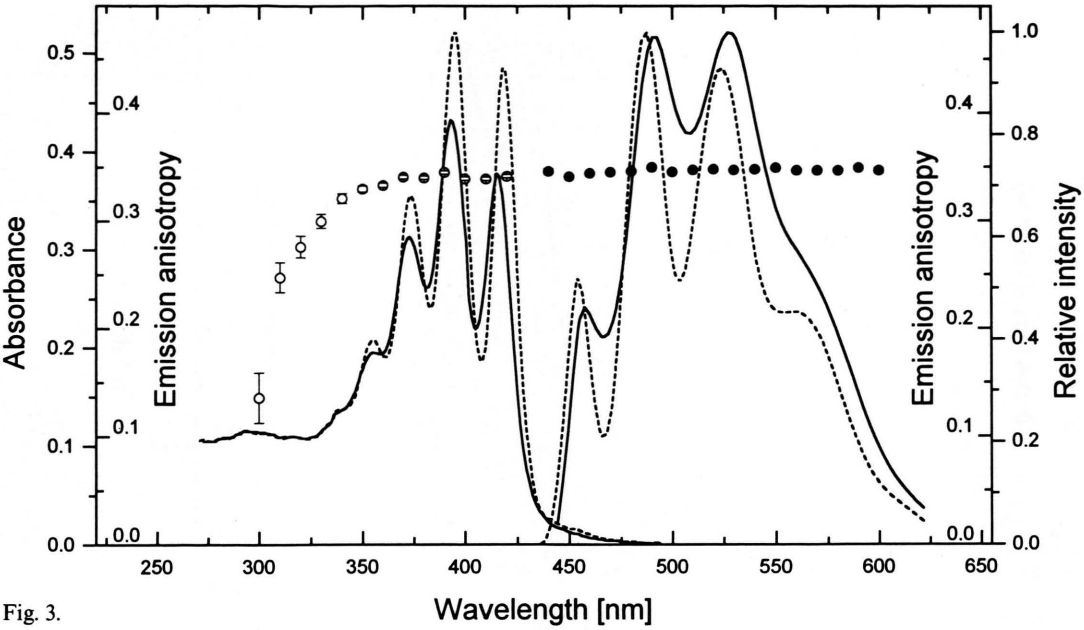

Fig. 3.

The preparation of the polymer films (PVCh, PVF, EtA and PVA) was described [18].

The methods of measuring the absorption and fluorescence spectra, and the quantum yields and emission anisotropies were described in [15–17]. Fluorescence decays were measured on a K 2 multifrequency cross-correlation phase and modulation fluorometer at the Biochemistry Department of the University of Ancona, Italy.

3. Results

3.1. Absorption, Fluorescence and Emission Anisotropy Spectra

Figures 1–3 show the absorption, fluorescence and emission anisotropy spectra of DPO in PVA films, measured at 296 and 87 K prior to heating (Fig. 1) and after heating to 373 K (Fig. 2) and 423 K (Figure 3). In the non-heated sample (Fig. 1), on the short-wave side of the absorption band of the all-*trans* conformer a very strong band with a maximum at 300 nm occurs, corresponding to the ground-state *cis* conformer. As a result of heating to 373 K the structured long-wave (350–440 nm) absorption band intensifies (Figure 2). Finally, upon heating to 423 K (Fig. 3), the long-wave band becomes fully developed while the short-wave band almost completely disappears. The spectrum of the emission anisotropy is very interesting. The emission anisotropy of the non-heated sample is close to 0.3, whereas after heating to 373 K it drops to 0.150 due to the softening of the PVA polymer. In the sample heated to 423 K the value of the emission anisotropy reaches 0.354, which, however, differs markedly from the fundamental value of 0.4.

Similar as with DPH in PVA heated to 423 K, no distinct dependence of the intensity distribution upon the excitation light wavelength is observed for the DPO sample in PVA heated to 423 K.

Figures 4–6 show the absorption, fluorescence and emission anisotropy spectra of DPO in PVCh (Fig. 4), PVF (Fig. 5) and EtA (Fig. 6) for non-heated samples and samples heated to 423 K. Unlike the non-heated samples of DPO in PVA, no effect of the excitation light wavelength on the intensity distrribution in the fluorescence band can be observed. The absorption and fluorescence spectra of DPO in PVCh, PVF and EtA heated to 423 K are the same as those of the non-heated samples. Thus, the temperature effect on the absorption and emission properties of DPO in PVA films does not occur in other polymers such as PVCh, PVF and EtA, in which a high fluorescence anisotropy, close to the fundamental value $r_0 = 0.4$, is observed: 0.391 and 0.389 for DPO in PVCh and EtA, respectively.

It should be pointed out that the polymers used have their own absorption in the short-wave region

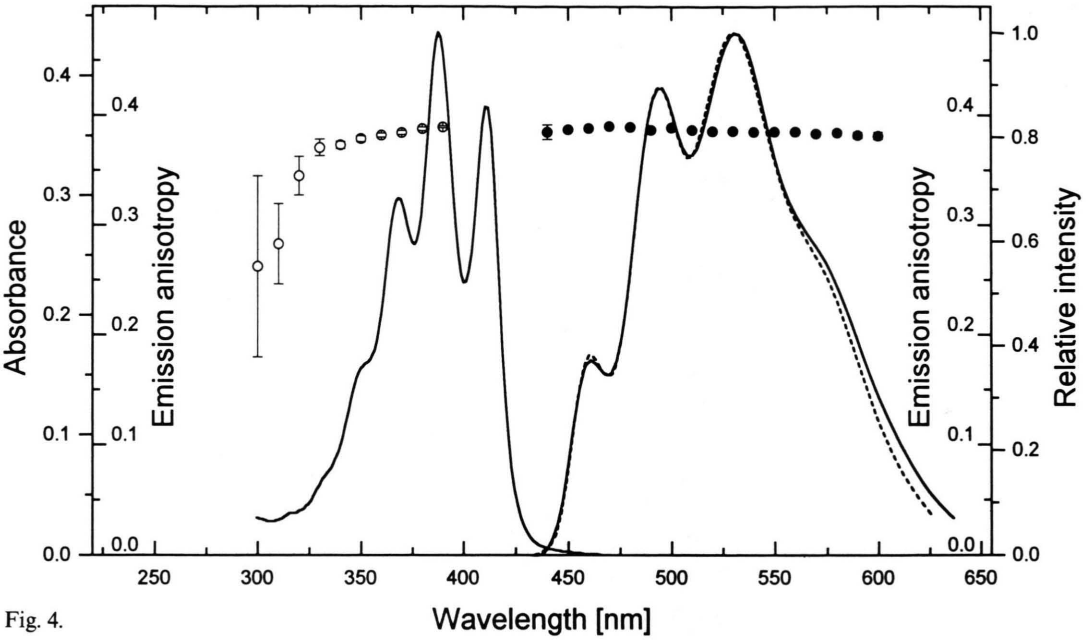

Fig. 4.

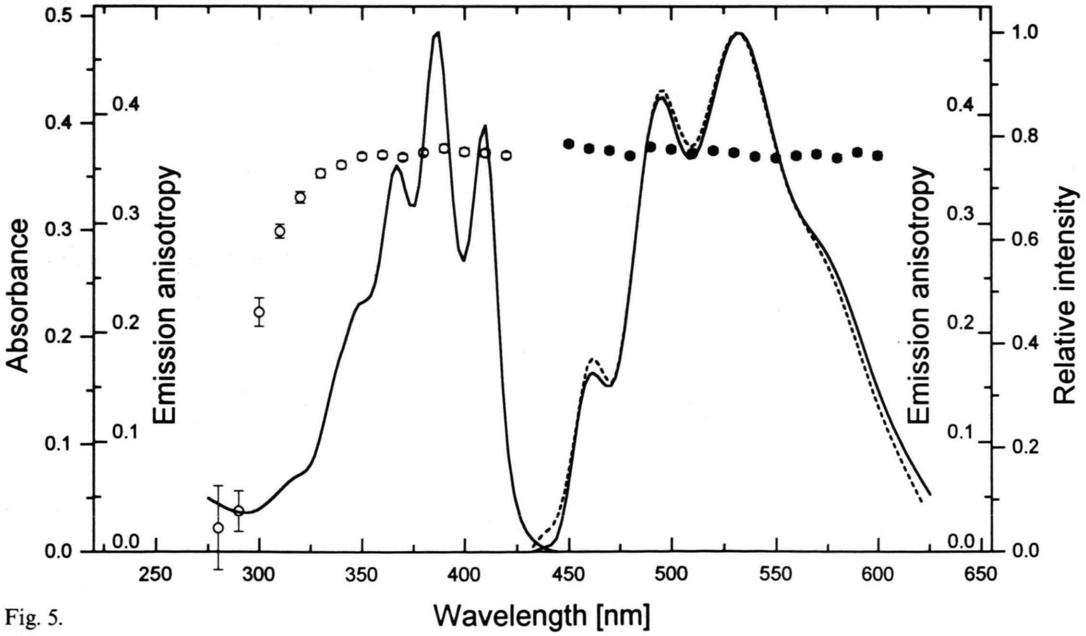

Fig. 5.

Figs. 4–6. Absorption and fluorescence spectra of DPO in PVCh (Fig. 4), PVF (Fig. 5), and EtA (Fig. 6) films measured at 296 K before (solid line) and after heating (dashed line). The fluorescence and emission anisotropy (●) spectra were obtained for $\lambda_{exc} = 390$ nm. ○ denote the emission anisotropy at $\lambda_{obs} = 483$ nm for various λ_{exc}.

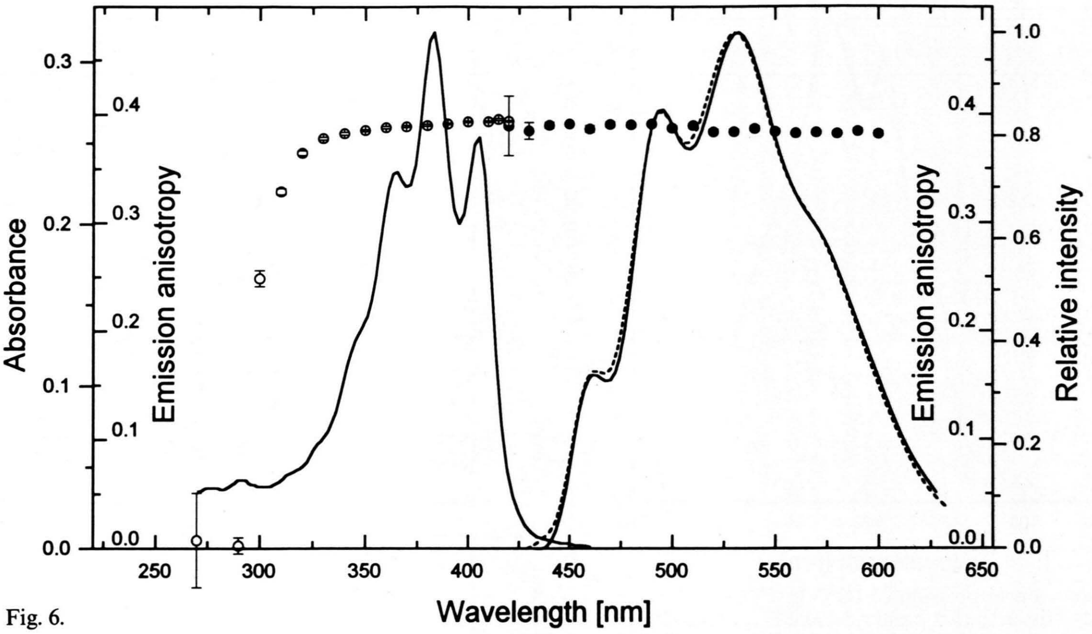

Fig. 6.

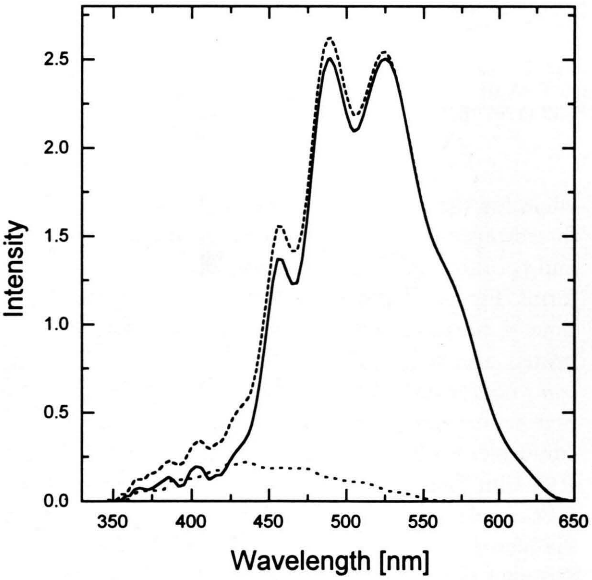

Fig. 7. Fluorescence spectrum of DPO in PVA film (dashed line) after heating to 423 K, measured at 296 K, and fluorescence spectrum of neet PVA film (dashed line). The solid line corresponds to the corrected spectrum.

and emit weak fluorescence. For example, Fig. 7 shows the global fluorescence spectrum of DPO in PVA heated to 423 K, the spectrum of PVA alone and the corrected spectrum. On the short-wave side of the main fluorescence band, a weak band can be observed. A similar band was recorded for DPO in non-heated PVCh films (solid line in Fig. 8) and EtA (dashed line). In all the three cases the excitation light wavelength, λ_{exc}, was 320 nm.

3.2. Fluorescence Quantum Yields and Lifetimes

As already shown in [16], the fluorescence quantum yield, Φ_F, grows dramatically upon heating the DPO sample in PVA to above 358 K. Table 1 summarizes the quantum yield values determined for DPO in different polymers either non-heated or heated to 423 K. In the case of DPO in PVCh, PVF and EtA (non-heated samples), Φ_F amounts to about 0.22, being very low for the non-heated DPO sample in PVA (0.03) and even lower than for DPO in cyclohexane and methanol. The values of Φ_F for DPO in PVCh, PVF and EtA heated to 423 K are almost the same as for the non-heated samples, while for the heated DPO in PVA a strong increase in Φ_F is observed, even to 0.32, which is markedly higher than the quantum yield in the remaining polymers.

Table 2 summarizes the fluorescence decay times, τ, of DPO measured at 296 K in methanol, in a methanol-water mixture and in different polymers. In methanol and non-heated PVCh and EtA films, a single exponential fluorescence decay, τ_1, was observed, corresponding to the all-*trans* conformer,

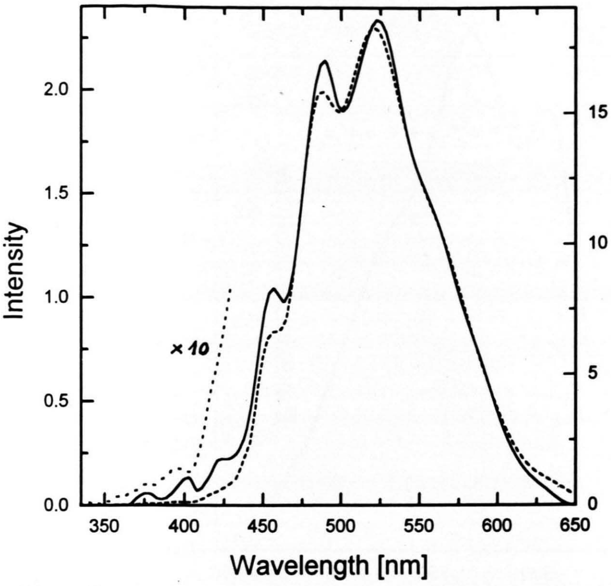

Fig. 8. Fluorescence spectrum of DPO in PVCh (solid line, the intensity axis on the left-hand side) and EtA (dashed lines, the intensity axis on the right-hand side) film at 296 K. The S_2 emission of DPO in EtA is shown in 10-fold scale of the fluorescence spectrum.

Table 1. Fluorescence quantum yields Φ_F of DPO in different polymers measured at 296 K.

DPO	Polymer			
	PVA	PVCh	PVF	EtA
before heating	0.03	0.22	0.20	0.22
after heating	0.32	0.25	0.19	0.20

Table 2. Values of fluorescence decay times of DPO in different media at 296 K.

Medium	λ_{exc} [nm]	λ_{obs} [nm]	τ_1 [ns]	A_1[a]	τ_2 [ns]	A_2[a]
Methanol	350	>420	5.35	1.00	–	–
Mixture of 50% methanol and 50% water	350	>420	4.50	0.90	0.001	0.10
PVCh	386	534	7.79	1.00	–	–
EtA	386	534	7.21	1.00	–	–
PVA (before heating)	375	>420	6.83	0.35	0.001	0.65
PVA (after heating)	375	>420	7.78	0.96	0.265	0.04

[a] $A_{1,2}$ are the preexponential factors (normalized relative fluorescence intensities, $A_1 + A_2 = 1$) representing the fractional contributions to the time-resolved decay of the components with a lifetime $\tau_{1,2}$.

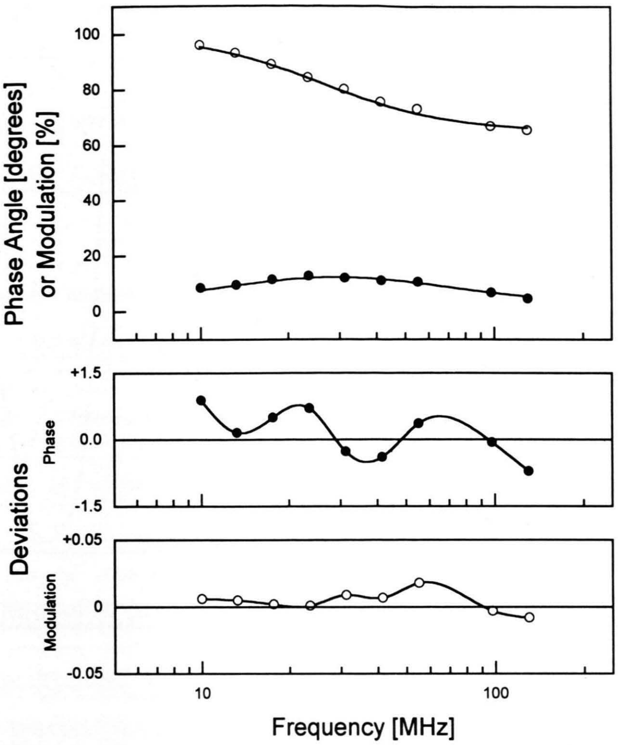

Fig. 9. Double exponential analysis of the emission of DPO in PVA film before heating. (●) and ○ denote experimental points for the phase angle and modulation, respectively.

while for the non-heated PVA a double exponential fluorescence decay was obtained with decay times τ_1 and τ_2 (Table 2), which evidences the emission of both forms. Figures 9 and 10 show the results of the decay time, τ, measurements carried out for DPO in non-heated and heated PVA film, respectively. The all-*trans* conformer with its longer decay time τ_1, in the non-heated film is less abundant (35%) than the *cis* conformer with its shorter lifetime τ_2 (65%). In the PVA film heated to 423 K, as many as 96% of the DPO molecules occur as all-*trans* conformers, with the lifetime τ_1 being the same as for the PVCh film. Stronger heating (to above 423 K), which might have transformed all the DPO molecules from the *cis* to the *trans* configuration, was not possible due to yellowing of the PVA film.

4. Discussion

The results obtained for DPO in different polymer films (PVCh, PVF and EtA) either non-heated or

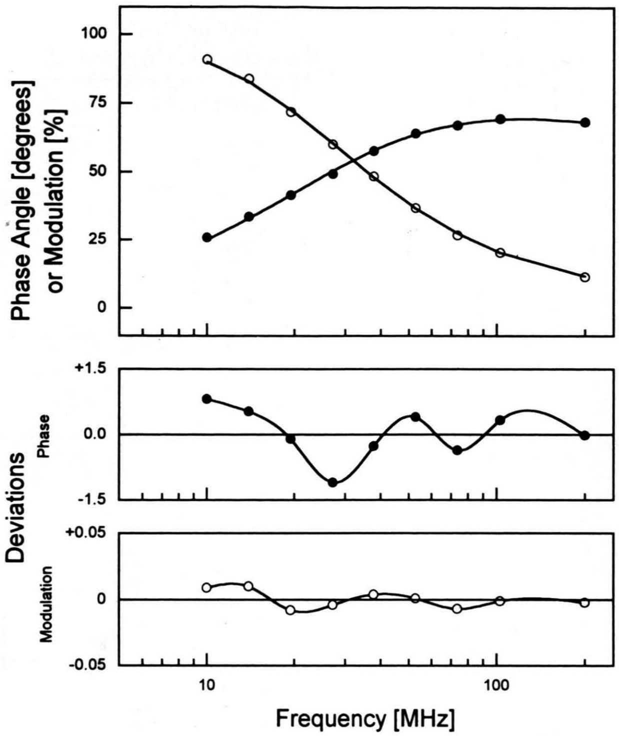

Fig. 10. Double exponential analysis of the emission of DPO in PVA film after heating. (●) and ○ denote experimental points for the phase angle and modulation, respectively.

heated to 423 K indicate, similar as for DPH [18], the occurrence of all *trans* conformers only. Unlike PVA, in polymers insoluble in water, no short-wave diffused band responsible for the absorption of the s-*cis* conformer can be observed at 296 K. In water-methanol mixture (Table 2), upon the 350 nm excitation and observation above 420 nm, a double exponential fluorescence decay occurs, whereas for methanol alone, a single exponential decay is found. Similar behaviour is observed for the PVA film either non-heated or heated. Heating to 423 K causes that as many as 96% of the molecules undergo transition to the all-*trans* configuration and only 4% remain as s-*cis* conformers. This problem was discussed in more detail in [18] for DPH in PVA and other polymers. Nonetheless, the following issues deserve attention.

As shown in Figs. 7 and 8, on the short-wave side of the strong fluorescence band a weak fluorescence band appears which probably corresponds to the transition from the $1^1B_u(S_2)$ level with a very short decay time. The very short emission decay time observed for DPO in water-methanol mixture and in the non-heated PVA film, amounting to 1 ps, cannot be attributed to the transition from the 1^1B_u level since the observation wavelengths were above 420 nm. Thus, also this fact supports the conclusion that the fluorescence of DPO in the PVA film, either non-heated or heated to 423 K, originates from all-*trans* and groundstate s-*cis* conformers, similar as observed for DPH [19].

The second problem is that the behaviour of the emission anisotropy varies in different polymers. In PVCh and EtA a value close to 0.4 is obtained, reflecting the enhanced rigidity of the microenvironment around the DPO molecules in these polymers. In PVA heated to 423 K, the emission anisotropy of DPO is distinctly different, amounting to 0.354. This results from a certain degree of orientational freedom of this molecule. Therefore also in this case isomerization can occur in the solid phase (PVA polymer), like e.g. in low-temperature n-alkane solutions of DPO [2]. In part VII of this series photoisomerization of diphenylpolyenes in PVA polymers will be dealt with.

Acknowledgements

This work was supported by Grant No. 2 0283 91 01 from the Committee for Scientific Research, Warsaw.

One of the authors (G.P.) wishes to thank Professor G. Curatola (Biochemistry Department, University of Ancona, Italy) for being awarded fellowship at her laboratory.

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